Applied Organometallic Chemistry (1988) 2 391–393
0268-2605/88/02416391/$03.50

SHORT REVIEW

Utilization of inorganic and organic arsenic compounds in new technologies

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Received 17 March 1988 Accepted 26 April 1988

This paper reviews the use of arsenic compounds in semiconductor manufacture and emphasizes the role of alkylated arsenic compounds.

Keywords: Arsenic compounds, semiconductors, chalcogen glasses, alkylarsenic compounds

INTRODUCTION

Arsenic compounds have been used for a long time as medicines, dyestuffs, agricultural chemicals, herbicides, pesticides, preservatives, and clarifiers for lead alloys and glasses. Approximately 30 000 tonnes of arsenic are now being consumed worldwide.

Certain arsenic compounds are highly toxic. For instance, arsenic trioxide caused many accidental and premeditated, often fatal, intoxications in man. Trivalent arsenic is known to interact with thiol groups in enzymes resulting in reduced activity or inactivation. The International Agency for Research on Cancer considers arsenic trioxide to be carcinogenic. The toxic properties of arsenic compounds and their use as homicidal agents have earned a sinister reputation for arsenic compounds generally.

Recently, arsenic compounds have become important starting materials for the fabrication of semiconductors, such as gallium arsenide (GaAs), and the preparation of arsenic-containing chalcogen glasses. Alkylarsenic compounds, such as trimethylarsine [$(CH_3)_3As$] and triethylarsine [$(C_2H_5)_3As$], are now being investigated as less toxic substitutes for arsine (AsH_3). Great progress is being made in the utilization of arsenic in the semiconductor and similar new materials industries.

This paper reviews the use of arsenic compounds in semiconductor manufactüre with special emphasis on alkylated arsenic compounds.

COMPOUND SEMICONDUCTORS INCLUDING GALLIUM ARSENIDE (GaAs)

Most semiconductors are based on silicon or germanium. Arsenic and arsine (AsH_3) are used to dope semiconductors, e.g. by high-temperature diffusion in epitaxial processes and by ion implantation. Binary compounds formed from a Group III (13) and a Group V (15) element are also semiconductors. Examples of such compounds are gallium arsenide (GaAs), gallium phosphide (GaP) and indium antimonide (InSb). Group III–V semiconductors have several advantages over silicon: they emit light, allow high-speed operation, function at temperatures up to 350°C, and respond to magnetic fields. Because Group III–V semiconductors emit light (silicon does not), light-emitting diodes (LED) and laser diodes (LD) can be constructed from them. By varying the wavelength of the emitted and received light through use of various types of elements, materials most suitable for optical fibers have been developed.

Gallium arsenide is the most important Group III–V semiconductor. The electron speed in gallium arsenide is six times higher than in silicon making gallium arsenide the preferred choice for the construction of fast computers and communication equipment. In addition, gallium arsenide exhibits semi-insulating properties, integratibility, low noise, low power consumption, and good resistance against damage by radiation.

GALLIUM ARSENIDE FILMS FROM ORGANOMETALLIC COMPOUNDS

Expitaxial growing techniques are important for the preparation of gallium arsenide. One of these, metallo-organic chemical vapor deposition (MOCVD), has been intensively studied in recent years. This method, proposed by Reukewin[1] in 1985, was pioneered by

Table 1 Organometallic and inorganic starting materials used by Manasevit *et al.*[2] for the preparation of III–V, II–VI and IV–VI compounds

Crystal	Material
II–VI (12–15)	
ZnS	$(C_2H_5)_2Zn,H_2S$
ZnSe	$(C_2H_5)_2Zn,H_2Se$
ZnTe	$(C_2H_5)_2Zn,(CH_3)_2Te$
CdS	$(CH_3)_2Cd,H_2S$
CdSe	$(CH_3)_2Cd,H_2Se$
CdTe	$(CH_3)_2Cd,(CH_3)_2Te$
IV–VI (14–16)	
PbTe	$(CH_3)_4Pb,(CH_3)_2Te$ $(C_2H_5)_4Pb,(CH_3)_2\ Te$
PbS	$(CH_3)_4Pb,H_2S$
PbSe	$(CH_3)_4Pb,H_2Se$
PbSnTe	$(CH_3)_4Pb,(C_2H_5)_4Sn;(CH_3)_2Te$
SnS	$(C_2H_5)_4Sn,H_2S$
SnSe	$(C_2H_5)_4Sn,H_2Se$
III–V (3–15)	
GaAs	$(CH_3)_3Ga,AsH_3$
GaP	$(CH_3)_3Ga,PH_3$
GaAsP	$(CH_3)_3Ga,AsI_3,PH_3$
GaSb	$(C_2H_5)_3Ga,(CH_3)_3Sb$
GaAsSb	$(CH_3)_3Ga,AsH_3,(CH_3)_3Sb$
AlAs	$(CH_3)_3Al,AsH_3$
GaAlAs	$(CH_3)_3Ga,(CH_3)_3Al,AsH_3$
GaN	$(CH_3)_3Ga,NH_3;(C_2H_5)_3GaNH_3$
AlN	$(CH_3)_3Al,NH_3$
InAs	$(C_2H_5)_3In,AsH_3$
InP	$(C_2H_5)_3In,PH_3$
GaInAs	$(C_2H_5)_3In,(CH_3)_3Ga,AsH_3$
InSb	$(C_2H_5)_3In,(C_2H_5)_3Sb$
InAsSb	$(C_2H_5)_3In,(C_2H_5)_3Sb,AsH_3$

Manasovit[2,3] for the growth of single crystals. Beginning in 1968 Manasovit succeeded in preparing Group III–V, II–VI, and IV–VI compounds (Table 1). Semiconductors may be prepared by reacting an organometallic compound with an inorganic compound or reacting two or more organometallic compounds. For example, trimethylgallium [$(CH_3)_3Ga$] and arsine (AsH_3) are introduced as gases in a hydrogen stream into a crystal-growing furnace, in which dimethylgallylarsine is formed as the intermediate that decomposes in a subsequent step on the surface of a heated substrate (Eqn 1). The formation of gallium arsenide is however believed not to be as simple as shown in Eqn. 1. More complex reactions may involve alkyl groups and hydrogen interacting on the surface of the substrate surface. Molecular beam epitaxy operates under ultrahigh vacuum, whereas MOCVD can be used under normal pressure.

$$\begin{array}{l} (CH_3)_3Ga + AsH_3 \rightarrow (CH_3)_2GaAsH_2 + CH_4 \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad GaAs + 2CH_4 \quad [1] \end{array}$$

The alkyl metal compounds to be used in MOCVD should be safe to store and handle at room temperature, should be liquid at this temperature, and should have a substantial vapor pressure. Compounds that meet these requirements are trimethylthallium [$(CH_3)_3Tl$]; dimethyl sulfide [$(CH_3)_2S$]; the dimethyl and diethyl compounds of zinc (R_2Zn) and mercury (R_2Hg); trimethyl- and triethyl-bismuth (R_3Bi); the fully alkylated compounds, R_nM ($R = CH_3$, C_2H_5, C_3H_7, C_4H_9), of cadmium ($n = 2$), of boron, aluminum, gallium and indium ($n = 3$), and of silicon, germanium, tin, and lead ($n = 4$); and the trialkyl compounds, R_3M ($R = CH_3$, C_2H_5, C_3H_7, C_4H_9), of phosphorus, arsenic and antimony.

For the preparation of crystalline films of gallium arsenide, trimethylgallium or triethylgallium have been used as the gallium-containing component and arsine, as the arsenic-containing component. Because arsine is very toxic[4] [lethal concentration (LC) 250 mg m^{-3}; the American Conference of Governmental Industrial Hygienists' Threshold Limit Value (ACGIH's TLV) is 0.05 ppm for time-weighted average], and a gas at room temperature, trialkylarsines have recently been intensively studied as a replacement for arsine. Trialkylarsines are less toxic, are liquids at room temperature and have a very strong garlic odor that makes them easily detectable at very low concentrations. The colorless liquids trimethylarsine (b.p. 53°C, density 1.310 g cm^{-3} at 2°C, n_D^{20} 1.4541) and triethylarsine (b.p. 37°C 15.5 Torr, density 1.0735 g cm^{-3} at 20°C, n_D^{20} 1.475) are much easier to handle than arsine.

Crystalline films of gallium arsenide were first grown from trialkylarsine in 1980. When trimethylarsine was used[5,6] the films were of inferior quality compared with those obtained from arsine. The cause for the observed difference in quality is not known. Impurities introduced with the organometallic compounds might be responsible. Triethylarsine, which does not decompose as easily as trimethylarsine, is said to reduce these carbon impurities in gallium arsenide.

Kamimoto *et al.*[7] grew crystalline films of gallium arsenide from trimethylgallium and triethylarsine and observed substantial amounts of impurities in the films. The concentration of impurities was high when the films were grown at higher temperatures. When tributylarsine and trimethylgallium were used, the gallium arsenide had fewer carbon inclusions than gallium arsenide prepared from other trialkylarsines. Experiments with tri(t-butyl)arsine produced evidence that pure gallium arsenide might be obtainable from reactions of trimethylgallium and trialkylarsines.[8]

With increasing demand for gallium arsenide the quantities of arsenic and arsenic compounds used in the manufacturing process will also increase. Adequate precautions must be taken to guard against exposure of workers to arsines and against pollution of the environment. Trialkylarsines, potential sources of arsenic for the preparation of gallium arsenide, are believed to be less toxic and therefore more desirable and safer for large-scale processes than arsine. However, reliable toxicity data substantiating this belief are not available.

Acknowledgements The author thanks K Takemoto, Sumitomo Electric Industries Ltd, S Ishiguro, Furukawa Mining Industries Ltd, and K Takamatsu, Tri Chemical Laboratory Inc, for helpful suggestions.

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